PATENT SPECIFICATION

NO DRAWINGS

922,458

Date of Application and filing Complete Specification: June 1, 1959.

No. 18639/59.

Application made in Germany (No. F25875 IVb/39c) on May 31, 1958.

Complete Specification Published: April 3, 1963.

Index at acceptance:—Class 2(6), G1(B1:C1), G2B, G3(A2:C2:C3), G4A.

International Classification:—C08f.

COMPLETE SPECIFICATION

Modified Polyvinyl Alcohols and process for preparing same

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a body corporate recognised under German Law, of Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to modified polyvinyl alcohols and a process for preparing same.

A number of processes for the manufacture of water-soluble modified polyvinyl alcohols are known. They consist essentially in

1) partially hydrolyzing or alcoholysing polyvinyl esters in an acid or alkaline medium. Polyvinyl acetate can, for example, be alcoholised in a manner such that 10 to 15% of residual units of acetate remain in the polyvinyl alcohol with retention of the solubility in water;

2) completely or partially hydrolyzing or alcoholysing copolymers of vinyl esters or such polyvinyl esters as contain relatively large amounts of residual catalyst.

Specification No. 818,037, for example, discloses the preparation of special highly viscous, soluble polyvinyl alcohols by hydrolysis of polyvinyl acetates which have been prepared in the presence of dioleyl peroxide.

Specification No. 857,147 describes the manufacture of highly viscous, soluble polyvinyl alcohols by hydrolysis of copolymers of vinyl acetate and vinyl ethers containing more than 6 carbon atoms.

It is also known to prepare modified polyvinyl alcohols by partially hydrolyzing copolymers of different vinyl esters with due regard to the different speeds of hydrolysis corresponding to the different ester groups as is possible, for example, when copolymers of vinyl formate and vinyl stearate are used.

3) reacting the polyvinyl alcohol with other reactive compounds either during hydrolysis or after its isolation.

A number of processes relating to this reaction, for example a partial acetalization or ketalization of the polyvinyl alcohol with an aldehyde or a ketone, have been described. This group of processes also comprises subsequent partial esterifications, for example cyano-ethylation and oxyethylation, esterifications.

The subsequent reactions of polyvinyl alcohol are in most cases complicated and expensive processes. The oxyethylation of polyvinyl alcohol has, for example, in some cases to be carried out under pressure in an autoclave. It is often difficult to separate residual excess of the catalyst or other reagents from the reaction mixture. The products are consequently in most cases discoloured and inhomogeneous.

The general technical purposes of the modification of polyvinyl alcohol are, for example, the modification of its viscosity properties, that is to say the viscosity of its solution in water, and its surface-active or interfacially active properties. The processes described in some patent specifications are also directed to the preparation of polyvinyl alcohols insoluble in water, which is of importance as regards the use of polyvinyl alcohol as a plastic.

A quite different object of the modification of polyvinyl alcohol is the preparation of a polyvinyl alcohol having a better solubility in water as is required, for example, in the packaging industry for the preparation of water-soluble packing materials. As is known, the commercial varieties of polyvinyl alcohol do not dissolve very rapidly in cold or hot water and often they do not quite dissolve completely.

Another object of the modification of polyvinyl alcohol is the plasticizing of the polyvinyl alcohol film, which is generally brittle

and to which a good and lasting plasticizing can be imparted only with difficulty.

It is known that polyvinyl alcohol is a good protective colloid as results from the determination of the so-called gold number. Polyvinyl alcohol is, however, not very surface-active. If 1% by weight of polyvinyl alcohol is dissolved in water, the value of the surface tension of water which is about 72 dynes/cm at 20°C. decreases to about 55 to 60 dynes/cm. An aqueous soap solution of 1% strength, on the other hand, has a surface tension of 28 to about 33 dynes/cm. Hence it follows that soap excels polyvinyl alcohol as regards surface-active properties. The surface-active properties of polyvinyl alcohol can be notably improved by modifying the latter with hydrophobic residues. If a polyvinyl alcohol containing 15% of propionyl or isobutyryl radicals is dissolved in water so as to yield a solution of 1% strength, the surface tension obtained amounts to about 37 or 32 dynes/cm, respectively.

The preparation even of small quantities and certainly of large quantities of polyvinyl alcohols containing residual acyl groups is not a simple process but a process necessitating the exact observation of strictly limited reaction conditions.

Products of the aforesaid kind are, of course, very valuable as regards their industrial use since they combine the properties of a good protective colloid with those of an extremely surface-active substance and this is very important, for example, when polyvinyl alcohol is used as a textile auxiliary, for example as a dressing agent, or when it is used as an emulsifier colloid in polymerization processes carried out in the aqueous phase.

According to the present state of the art the improvement of the surface-active properties of polyvinyl alcohol by an increased introduction of hydrophobic groups is limited since the solubility of such products in water soon decreases. It is known, for example, that the product obtained by hydrolyzing a copolymer of vinyl acetate with only a relatively small quantity of ethylene is insoluble in water.

If the content of free hydroxyl groups in the polyvinyl alcohol is decreased the latter may still be soluble in cold water but when a solution thus obtained which is at first clear is heated, phenomena of flocculation soon occur. The temperature at which the first flocculation phenomena can be observed is called the turbidity point. Due to these phenomena of flocculation the application of modified polyvinyl alcohols having improved surface-active properties is, of course, considerably limited. Polyvinyl alcohols of this kind are, for example, not suitable for use in polymerization reactions conducted in the aqueous phase at elevated temperatures. Polyvinyl alcohols containing 40% of residual acetate units dissolve in water only at room temperature and they already precipitate at a temperature of only 35°C. (cf. Kainer, "Polyvinylalkohole", page 43, Stuttgart, 1949). The turbidity point of polyvinyl alcohols containing 15% of propionyl radicals and having a solution viscosity of about 80 centipoises (determined in a solution of 4% strength in water at 20°C.) is about 50°C.; polyvinyl alcohols containing 7% of propionyl radicals and having a viscosity of 30 to 40 centipoises have a turbidity point of 65°C. The situation is even more unfavourable if the polyvinyl alcohol contains longer organic residues, for example stearyl residues.

The plasticizing of polyvinyl alcohol is in general brought about externally, for example by means of glycerol. The external plasticizing has, however, considerable disadvantages which are due to the migration of the plasticizer which occurs especially readily in the case of polyvinyl alcohol. For the reasons that have already been mentioned, it has hitherto been impossible to bring about a so-called "internal plasticizing" of polyvinyl alcohol by means of the corresponding copolymers which are used as starting material or by subsequent reactions, for example oxyethylation, in a satisfactory way.

The present invention is based on the observation that modified water-soluble polyvinyl alcohols (as hereinafter defined) having improved properties can be prepared in a very simple manner by subjecting graft-polymers which have been prepared in the homogeneous phase, for example by the process described in Specification No. 12886/59 (Serial No. 922,457), from vinyl esters and polyalkylene glycols, to an alkaline or acid hydrolysis or alcoholysis, using a method known *per se*.

By modified polyvinyl alcohols obtained by the process of the invention are to be understood water-soluble polymeric compounds constituted by at least 50% by weight of units of the formula

$$-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-.$$

The hydrolysis is carried out, either partially or completely, in batches or continuously, in known manner in the presence of solvents or mixtures of solvents, for example methanol or a mixture of methanol with methyl acetate, and, if desired, in an inert atmosphere, for example, in the presence of nitrogen.

When an alkaline hydrolysis or alcoholysis is carried out, the catalyst is, for example, an alkali metal hydroxide, preferably sodium or potassium hydroxide, dissolved in methanol. In general it suffices to add the alkali metal in a catalytic amount. The addition, for example, of 0.2 to 5.0% by weight of sodium hydroxide, calculated on the polymer to be hydrolyzed, is sufficient. It is, however, also

possible to add larger quantities, for example molar quantities. The hydrolysis may be carried out at room temperature, for example at 20°C., or at higher temperatures, for example at the boiling temperatures of the solvent or solvents, for example at 57°C. The hydrolysis or alcoholysis in the presence of an acid is carried out, for example, by means of the usual mineral acids, for example sulphuric acid or hydrochloric acid. This operation is usually carried out at the boiling temperature of the solvent, it may, however, also be carried out at lower temperatures, for example at a temperature within the range of 20 to 30°C.

The graft polymers used as starting materials in the process of the invention are prepared by the process described in Specification No. 12886/59 (Serial No. 922,457) mentioned above by polymerizing vinyl esters, for example vinyl acetate, vinyl propionate, vinyl butyrate or vinyl stearate, preferably vinyl acetate, in homogeneous phase, alone or in admixture with one another in the absence or presence of other copolymerizable compounds, in the presence of polyalkylene glycols or their derivatives, and, if desired, also using solvents. As polyalkylene glycols suitable for use in the process of the invention there may be mentioned by way of example polyethylene glycols, polypropylene glycols and the other homologues having a molecular weight within the range of about 400 to several millions, oxyethylated polypropylene glycols and derivatives of the aforesaid compounds, for example polyalkylene glycols, one or both terminal hydroxyl groups of which are etherified or esterified and polyalkylene glycols, one or both hydroxyl groups of which are substituted by mono- or polyfunctional amines or amides, and the reaction products of polyalkylene glycols with mono- or polyisocyanates.

The graft polymers used as starting materials in the process of the invention contain about 0.1 to about 50% by weight, preferably 0.1 to 20% by weight of the above-mentioned polyalkylene glycols which are chemically bound and which are present in the said polymers either alone or in admixture one with another.

The quantities of polyalkylene glycol or glycols which have been bound in the graft polymer used as starting material are completely preserved in the hydrolysis product. It was not at all to be foreseen that the structure of the graft polymer used as starting material would be preserved when the polymer was subjected to a chemical reaction, for example hydrolysis or alcoholysis.

Due to the large number of graft polymers that may be used as starting materials, it is possible to prepare polyvinyl alcohols which have a variety of new and interesting properties.

The various methods that are known for carrying out an alkaline or acid hydrolysis or alcoholysis of polyvinyl esters and which are also applicable to the above-mentioned graft polymers, offer further possibilities of modifying the properties of polyvinyl alcohols. The methods for a partial acid or alkaline hydrolysis may also be applied.

The new modified polyvinyl alcohols are colourless or only slightly coloured loose powders which can easily be dissolved in water.

Polyalkylene glycols, especially polyethylene glycol and its derivatives, have the general property of being soluble in alcohols and of being at the same time hydrophilic. This property is imparted to a certain extent to the graft polymers and accordingly to the hydrolysis products obtained from the graft polymers.

This property involves a technical advantage even as regards the hydrolysis process, since the viscosities of the reaction mixtures obtained by the hydrolysis of graft polymers are far smaller than the temporarily high viscosity of the hydrolysis or alcoholysis mixtures of ordinary polyvinyl esters which leads to the formation of the so-called thick phase.

In order to suppress this highly viscous phase it has hitherto been necessary to use agitators having extraordinarily strong driving mechanisms or to add certain solvents, for example gasoline, to the reaction mixtures. The addition of these solvents necessitates a subsequent fractional distillation of solvent for recovery. Both measures have hitherto much increased the cost of the preparation of polyvinyl alcohol.

The hydrophilic properties of the polyalkylene glycols contained in the hydrolysis products obtained by the process of the invention improve the solubility in water of the hydrolysis products. For example, when a graft polymer is partially hydrolyzed or hydrolyzed and simultaneously or subsequently partially acetalized by one of the known methods mentioned above, products are formed which are completely soluble in water even in cases in which corresponding hydrolysis products obtained from ordinary polyvinyl esters exhibit phenomena of turbidity and flocculation in water at an elevated temperature.

In this connection it should be mentioned that the rate of solution in water of the new modified polyvinyl alcohols is high as compared to the rate of solution of the polyvinyl alcohols or derivatives thereof which have hitherto been known. This is another technical advantage.

For the reasons that have already been mentioned, the new modified polyvinyl alcohols are used with special advantage as surface-active and interfacially active substances and as protective colloids, for

example as emulsifiers for dispersion polymerization.

With regard to the use of the new products as surface-active agents it must also be mentioned that polyvinyl alcohols, preferably those containing polypropylene glycols or their derivatives in a chemically bound form, are excellent surface-active protective colloids. For example, at 20°C. in an aqueous solution of 1% strength, a polyvinyl alcohol containing 20% by weight of residues of polypropylene glycol having a molecular weight of 2,000 reduces the surface tension of the water to about 37 dynes/cm (the initial value of the surface tension of the water being 72 dynes/cm), whereas an aqueous solution of 1% strength of a polyvinyl alcohol containing 15% by weight of residual acetyl groups reduces the surface tension of the water only to about 45 dynes/cm. Moreover, the preparation of the first-mentioned polyvinyl alcohol is much easier than that of the polyvinyl alcohol containing acetyl groups.

Another technical advantage of the process of the invention is that foils prepared from polyvinyl alcohols which preferably contain chemically bound long-chain polyalkylene glycols, are softer when exposed to air than the corresponding usual foils of polyvinyl alcohol. A small quantity of water which is bound very firmly like oxonium to the units of the polyglycollic ether contained in the modified polyvinyl alcohols obtained by the process of the invention and which cannot easily be removed by usual drying, can be regarded as an efficient "plasticizer" for the foils prepared from the aforesaid modified polyvinyl alcohols. Moreover, the new modified polyvinyl alcohols retain an additional plasticizer which is usually glycerol or glycol more firmly than the polyvinyl alcohols which have hitherto been known were able to do. The disadvantages of a migration and the volatility of the plasticizer are thus avoided to a large extent.

Such soft types of polyvinyl alcohol are very valuable as regards use for technical purposes; they constitute, for example, a valuable material for the preparation of water-soluble packing foils.

Modified polyvinyl alcohols may be used above all as sizing and finishing agents in the industry of textile auxiliaries; in addition they may be used for the preparation of cosmetic articles.

To sum up: The process according to the invention offers the following technical advantages and the new modified polyvinyl alcohols have the following properties:

1) The formation of the "thick phase" occurring during the hydrolysis or alcoholysis is reduced;

2) the water-solubility, especially that of polyvinyl alcohols containing organic (hydrophobic) residues, is improved;

3) the rate of solution in water is increased;

4) it is possible to prepare well plasticized foils of polyvinyl alcohol;

5) a wide variety of properties may be attained due to the many possibilities of applying the numerous known methods of preparing polyvinyl alcohol or modified polyvinyl alcohols to the preparation of hydrolysis products from graft polymers which can in their turn be prepared in various ways;

6) the modified polyvinyl alcohols can be prepared in a particularly simple way, they have a good effect as protective colloids, a good surface-activity and no or only a high point of turbidity.

Specification No. 874,130 describes and claims a process for preparing a hydrolyzed derivative of a copolymer of vinyl acetate and a polyoxyalkylene compound as defined comprising preparing a copolymer by the process claimed in any of Claims 4 to 7 dissolving the copolymer in methanol or ethanol mixing with the resultant solution an alkaline alcoholysis catalyst for polyvinyl acetate and recovering the resultant hydrolyzed product.

The term "polyoxyalkylene" compound is defined in that Specification as meaning polyethylene glycol; polypropylene glycol; polybutylene glycol; a block copolymer of ethylene glycol and propylene glycol; a monoether of a lower alkyl alcohol with any of the said glycols or block copolymers, or a monoester of an aliphatic carboxylic acid with any of said glycols or block copolymer.

No claim is made herein to the process claimed in claim 8, of Specification No. 874,130, or to a copolymer of vinyl alcohol and a polyoxyalkylene compound as defined in that Specification.

The following Examples illustrate the invention, the parts being by weight:

EXAMPLE 1.

Preparation of a polyvinyl alcohol containing units of polyethylene glycol;

The graft polymer used as starting material was prepared in the manner described in Specification No. 12886/59 (Serial No. 922,457).

In a glass bottle provided at its top with a reflux condenser and with a dropping funnel, 5 to 10 parts of a solution consisting of

89 parts of vinyl acetate,
10 parts of polyethylene glycol having a molecular weight of about 4,000 and
1 part of dibenzoyl peroxide were polymerized by being heated on a water bath at 80°C.

After the beginning of the polymerization, the rest of the solution was added drop by drop within about 2 hours. When the introduction of the polymerization mixture was

complete, the temperature of the bath was increased for 1 to 2 hours to 90°C. During this time the reflux ceased and the polymerization was completed. Monomer that had not undergone conversion was then eliminated at the aforesaid temperature by applying a pulsating vacuum.

97 parts of a glass-clear graft polymer having a K value (according to Fikentscher, "Cellulosechemie" *13*, 58 (1932)) of 42 (determined as a solution of 1% strength in ethyl acetate) and containing 5% by weight of bound oxyethyl groups were obtained.

Hydrolysis or alcoholysis:

A solution of

565 parts of the graft polymer described above in 1695 parts of methanol and
753 parts of petroleum ether (boiling range 60 to 90°C.) was added at 20°C. while stirring to
168.7 parts of methanolic sodium hydroxide solution of 15% strength by weight

which were contained in an enamelled vessel heated by means of a water bath and provided with a horseshoe stirrer, a reflux condenser and a thermometer.

The stirring of the mixture was continued for 3 hours at 20°C., the resulting product was separated by filtration from the mother liquor, washed several times with methanol and dried in a vacuum drier at 40°C. 270 parts of a water-soluble white powder having a K value of 47 (determined as a solution of 1% strength in water) and containing 0.9% by weight of residual acetyl groups were obtained. The content of oxyethyl which was determined by the method according to Morgan (cf. P. W. Morgan, Ind. Engng. Chem., 18, 500 (1946)) amounted to 10.8% by weight. Under the same conditions the product dissolved in water about 3 times as quickly as a usual polyvinyl alcohol of the same K value.

EXAMPLE 2.

Preparation of a polyvinyl alcohol containing units of polyethylene glycol.

The graft polymer used as starting material was prepared in the manner described in the first part of Example 1 from

89 parts of vinyl acetate,
10 parts of polyethylene glycol having a molecular weight of 25,000 and
1 part of dibenzoyl peroxide.

The glass-clear product had a K value of 56 and contained 9% by weight of chemically bound oxyethyl groups.

The hydrolysis or alcoholysis was carried out in the same apparatus and in the same manner as in Example 1.

Solution contained in the apparatus:

280 parts of a methanolic solution of sodium hydroxide of 15% strength by weight.

A solution of

1,000 parts of the graft polymer described above in 4,000 parts of methanol and
1,670 parts of petroleum ether (boiling range 60 to 90°C.) was added.

The hydrolysis mixture was stirred for another 4 hours at 20°C. and then worked up as described in Example 1.

455 parts of a water-soluble white powder containing 0.5% by weight of residual acetyl groups were obtained. The oxyethyl content amounted to 17% by weight.

The rate of solution in water of this product was about 3 times as high as the rate of solution of ordinary polyvinyl alcohol having the same K value, the rate of solution being measured in both cases under the same conditions.

EXAMPLE 3.

Preparation of a polyvinyl alcohol containing units of polyethylene glycol by acid hydrolysis or alcoholysis:

The apparatus was the same as that used in Example 1.

740 parts of the graft polymer of vinyl acetate on polyethylene glycol having a molecular weight of 25,000, which graft polymer is described in the first part of Example 2,

were dissolved in

950 parts of methanol and
425 parts of methyl acetate.

32.75 parts of sulphuric acid of 78% strength by weight in 32.75 parts of methanol

were introduced into the above-mentioned solution.

The mixture was stirred at a rate of 40 revolutions per minute, the temperature of the water bath being 54°C. After 12 hours the hydrolysis was complete, the product was filtered off, washed with methanol until free from acid and dried in vacuo at 40°C.

295 parts of a white, water-soluble powder having a K value of 80 and containing 0.9% by weight of residual acetyl groups and 17% by weight of oxyethyl were obtained.

EXAMPLE 4.

Direct preparation of an aqueous solution of a polyvinyl alcohol containing units of polyethylene glycol:

Apparatus: Enamelled vessel on a water-

bath, provided with a stirrer and with a reflux condenser capable of being transformed into a distilling condenser, a thermometer and an inlet tube for steam so that a steam distillation could be carried out.

1,330 parts of a graft polymer that had been prepared in the manner described in the first part of Example 1 from 80% by weight of vinyl acetate on 20% by weight of polyethylene glycol of a molecular weight of 25,000 and which had a K value of 54, were dissolved in 5,310 parts of methanol and the resulting solution was introduced into a solution of

372 parts of a methanolic sodium hydroxide solution of 15% strength by weight.

Hydrolysis was brought about within 3 hours while stirring at 20°C. After the refluxing operation had been changed to a distillation operation, the methyl acetate that had formed was separated by distillation from the reaction mixture at a water bath temperature of 65°C. Subsequently the whole of the methanol present was expelled, while stirring, by direct introduction of steam. At the same time an aqueous solution of the polyvinyl alcohol that had formed was obtained. The solution was filtered while hot through a pressure filter. It contained 15% by weight of dry substances.

Example 5.

Preparation of a polyvinyl alcohol containing units of polyethylene glycol from a graft polymer of vinyl propionate:

The apparatus and the mode of operation were the same as those of Example 1.

Solution present in the apparatus:

42.5 parts of methanolic sodium hydroxide solution of 15% strength by weight.

A polymer solution consisting of

146.0 parts of a graft polymer prepared as described in the first part of Example 1 from vinyl propionate and polyethylene glycol of a modecular weight of 4,000 and containing 6% by weight of chemically bound oxyethyl groups and having a K value of 47

in 583.0 parts of methanol and

253.0 parts of petroleum ether (boiling range 60 to 90°C.) was added.

The hydrolysis mixture was stirred for 6 hours at 20°C. When worked up as described in Example 1 the mixture yielded a polyvinyl alcohol containing 1.5% by weight of residual propionyl groups and 11.5% by weight of oxyethyl.

Example 6.

Preparation of a polyvinyl alcohol containing units of polypropylene glycol.

A graft polymer was prepared from vinyl acetate, polypropylene glycol of a molecular weight of 2,000 and dibenzoyl peroxide according to the process described in Specification No. 12886/59 (Serial No. 922,457). 10 parts of polypropylene glycol having a molecular weight of 2,000 and 1 part of dibenzoyl peroxide were dissolved in 89 parts of vinyl acetate and polymerized at a temperature within the range of 75 to 80°C. in an appropriate vessel provided with a reflux condenser in a manner such that first 5 to 10% by weight of the reaction mixture were introduced into the vessel and after the beginning of the polymerization the remaining 95 to 90% by weight of the polymerization mixture was then added within about 2 hours. Soon after the introduction of the monomer was completed the reflux also ceased. In order to complete the polymerization the temperature was increased for 2 hours to 90°C. and the monomer that had not undergone conversion was then eliminated in a pulsating vacuum.

About 97 parts of graft polymer were obtained. The graft polymer had a K value of about 37 and a relative viscosity of 1.47, both values being determined in a solution of 1% strength by weight in ethyl acetate.

Hydrolysis or alcoholysis:

In a vessel provided with a suitable stirrer 170 parts of methanolic sodium hydroxide solution of 15.5% strength by weight were diluted with four times their weight of methanol.

600 parts of the graft polymer prepared in a manner described in the beginning of this example were dissolved in 2,400 parts of methanol and the resulting solution was introduced at room temperature in four portions, while stirring, into the aforesaid methanolic sodium hydroxide solution. Each of the 4 portions was introduced in the course of ½ hour. The interval comprised between the end of the introduction of one portion and the beginning of the introduction of the next portion was likewise ½ hour. After the introduction of the last portion the whole was stirred for another 4 hours.

The polyvinyl alcohol that had precipitated was filtered off with suction, washed with methanol until free from alkali and dried at 50°C. in a vacuum drier until its weight was constant. There were obtained 410 parts of a colourless fine-grained polyvinyl alcohol whose viscosity amounted to 4.3 centipoises in an aqueous solution of 4% strength by weight and to 6.5 centipoises in an aqueous solution of 5% strength by weight. At 20°C. the surface tension of an aqueous solution of 1% strength by weight of the polyvinyl alcohol

obtained was 38 to 39 dynes/cm. When heated to 100°C. the polyvinyl alcohol did not exhibit any phenomena of flocculation.

The following table indicates the values obtained by the analysis of the product obtained by the above-described experiment and the corresponding values of a normal saponified polyvinyl alcohol. (The products used for analysis were purified by dissolving them in water and reprecipitating with acetone (three times).)

	Ordinary polyvinyl alcohol	Graft polyvinyl alcohol
Content of C	54.6%	53.6%
Content of H	9.1%	9.0%
Content of OH	38.64%	34.9%

The product obtained by this experiment contained about 1% by weight of residual acetyl groups and had a K value of 42, determined in an aqueous solution of 1% strength by weight.

EXAMPLE 7.

Preparation of a polyvinyl alcohol containing units of oxyethylated polypropylene oxide.

A graft polymer was prepared from 10 parts of an oxyethylated polypropylene oxide (molecular weight: 4,500; hydroxyl value: 25; content of ethylene oxide: about 75% by weight), 1 part of dibenzoyl peroxide and 89 parts of vinyl acetate in the manner described in the first part of Example 1. The polymer so obtained had a K value of about 40.

In order to alcoholyse the product, 700 parts of it were dissolved in 2,800 parts of methanol and the alcoholysis was brought about in a manner analogous to that of Example 1 with 200 parts of methanolic sodium hydroxide solution of 15.7% strength by weight.

The polyvinyl alcohol thus obtained had the following values:

1) K value: 41;
2) viscosity in an aqueous solution of 4% strength by weight: 4.4 centipoises;
3) viscosity in an aqueous solution of 5% strength by weight: 6.7 centipoises;
4) surface tension of an aqueous solution of 1% strength by weight at 20°C.: 47 dynes/cm;
5) phenomena of flocculation when an aqueous solution was heated up to 100°C.: none.

By analysis the following values were found:

	Normal polyvinyl alcohol	Graft polyvinyl alcohol
Content of C	54.6%	52.8%
Content of H	9.1%	9.0%
Content of OH	38.64%	32.3%

Content of residual acetyl groups: about 1% by weight.

Content of oxyethyl groups determined according to Morgan 7.0% by weight (calculated as OC_2H_4).

It should also be mentioned that when graft polymers are used in a alcoholysis of this kind in which the whole of the hydrolysis solution is admixed in one operation with the whole of the catalyst solution, the increase of the viscosity of the reaction mixture is very small as compared to the increase of the viscosity of a reaction mixture of pure polyvinyl acetate having a K value of 40 and which is alcoholysed under the same conditions. In the latter case part of the reaction takes place in a very highly viscous phase.

EXAMPLE 8.

Preparation of a polyvinyl alcohol containing units of polyethylene glycol whose terminal hydroxyl groups have been reacted with a di-isocyanate:

The graft polymer used as starting material was prepared in the manner described in the first part of Example 1 from

175 parts of vinyl acetate,
25 parts of polyethylene glycol whose terminal hydroxyl groups had been reacted with toluylene-diisocyanate; molecular weight greater than 30,000, and
2 parts of dibenzoyl peroxide.

113 parts of the graft polymer thus obtained were dissolved in 339 parts of methanol and 151 parts of petroleum ether (boiling range 60 to 90°C.), filtered and introduced into 33 parts of a methanolic sodium hydroxide solution of 15% strength by weight and the experiment was continued in the manner described in Example 1. 52 parts of a polyvinyl alcohol powder that was readily soluble in water were obtained.

EXAMPLE 9.

Preparation of polyvinyl alcohol containing units of polyethylene glycol and having subsequently been subjected to a partial cyanoethylation:

Apparatus: Vessel provided with stirrer, reflux device and distillation device and heated by means of a water bath.

422 parts of acrylonitrile and
49 parts of an aqueous sodium hydroxide solution of 30% strength by weight

were added, while stirring, at 20°C. to
4,330 parts of an aqueous solution of 15% strength by weight of a hydrolyzed graft polymer prepared as described in Example 4.

The mixture was kept for 20 hours while stirring at 35°C. Then the solution was neutralized with phosphoric acid of 85% strength by weight.

In order to eliminate the residues of acrylonitrile that had not undergone conversion, the content of the vessel was quickly heated to 95°C. and steam was introduced into the reaction mixture until the steam distillate that passed over did not contain any more acrylonitrile (about 30 minutes).

A polymer solution containing about 14% by weight of dry substances was obtained. The plastic film obtained by drying the aforesaid solution contained 7% by weight of chemically bound nitrogen in addition to small quantities of salts.

The solution could be further used as a valuable textile auxiliary. In this case the residues of neutral salts are not disturbing, in some cases they are even desirable.

EXAMPLE 10.

Preparation of a polyvinyl alcohol containing units of polyethylene glycol having a particularly high molecular weight:

The graft polymer used as starting material was prepared by the solution polymerization of

90 parts of vinyl acetate and
10 parts of polyethylene glycol having a molecular weight greater than 1,000,000
in 75 parts of methanol and
1 part of diacetyl peroxide.

The mixture so obtained was stirred for 3 hours at 70°C. until the polymerization was complete. The solution was then poured into water and the polymer that had precipitated was filtered off with suction, washed well with water, dissolved once more in methanol, again precipitated with water, filtered off with suction and dried in vacuo at 50°C.

The graft polymer had a K value of 42 and contained 9% by weight of chemically bound oxyethyl groups.

The hydrolysis or alcoholysis was brought about in the manner described in Example 1.

Solution introduced into the vessel before the beginning of the reaction:

15.1 parts of sodium hydroxide solution of 15% strength by weight in methanol.

Polymer solution:

54.0 parts of the graft polymer described above in
216.0 parts of methanol and
90.0 parts of petroleum ether (boiling range 60 to 90°C.).

The hydrolysis product thus obtained was washed with methanol until free from alkali and it was then dried in a vacuum drier at 40°C.

A modified polyvinyl alcohol having a K value of 66 was obtained.

The portion of remaining acetyl groups amounted to 0.4% by weight and that of chemically bound oxyethyl groups to 17% by weight.

EXAMPLE 11.

Preparation of a vinyl alcohol copolymer containing units of polyethylene glycol:

In the manner described in Example 1 a graft polymer was prepared from

90 parts of vinyl acetate,
90 parts of vinyl propionate,
20 parts of polyethylene glycol having a molecular weight of 4,000 and
2 parts of dibenzoyl peroxide.
141 parts of the graft polymer so obtained were dissolved in
424 parts of methanol and
188 parts of petroleum ether (boiling range 60 to 90°C.) and introduced into
42 parts of methanolic sodium hydroxide solution of 15% strength by weight.

The mixture was worked up as described in Example 1.

55 parts of a modified water-soluble poly-

vinyl alcohol containing 13% by weight of oxyethyl groups were obtained.

EXAMPLE 12.

Preparation of a partially hydrolyzed polyvinyl acetate containing units of polyethylene glycol:

As starting material there was used the graft polymer prepared in the manner described in Example 1 from vinyl acetate and polyethylene glycol having a molecular weight of 4,000.

480 parts of the graft polymer so obtained were dissolved in 2,893 parts of methanol and
800 parts of petroleum ether (boiling range 60 to 90°C.).

12 parts of methanolic sodium hydroxide solution of 20% strength by weight in 600 parts of methanol were introduced at 20°C. into the aforesaid solution of the graft polymer while stirring slowly.

After 2½ hours exactly, the reaction mixture was neutralized by the introduction of 2N-acetic acid. The product was separated from the mother liquor by centrifuging, washed several times with methanol and dried in vacuo at 35°C.

The product had a K value of 44. It contained 9.8% by weight of residual acetyl groups and 10.2% by weight of bound oxyethyl groups.

The following table comprises the values of surface-tension (σ) in water at 20°C. and the turbidity point (measured in a solution of 1% strength by weight with the addition of 2 cc. of common salt solution of 20% strength by weight) of the modified polyvinyl alcohol and, for purposes of comparison, of a corresponding partially hydrolyzed polyvinyl alcohol having the same K value but containing no bound oxyethyl groups.

	σ in a solution of 4% strength	6 in a solution of 5% strength	turbidity point
modified polyvinyl alcohol	45	46	72°C.
Comparison polyvinyl alcohol	45	47	31°C.

EXAMPLE 13.

Preparation of polyvinyl alcohol containing units of oxyethylated nonyl phenol:

In the manner described in the first part of Example 1 a graft polymer was prepared from

89 parts of vinyl acetate,
10 parts of oxyethylated nonyl phenol (formed by oxyethylation of 1 mole of nonyl phenol with 45 moles of ethyl oxide)
1 part of dibenzoyl peroxide.

The graft polymer that had three times been precipitated with water from a methanolic solution had a K value of 37 and containing 2.5% by weight of bound oxyethyl groups and 48.5% by weight of acetyl residues.

Hydrolysis or alcoholysis:—

44.6 parts of the above-mentioned graft polymer dissolved in
178.4 parts of methanol

were introduced at 20°C. while stirring into a solution of

12.5 parts of methanolic sodium hydroxide solution of 15% strength by weight.

The mixture was stirred for another 3 hours. The product was then filtered off with suction from the mother liquor, washed with methanol until free from alkali and dried in vacuo at 35°C.

A modified, very readily water-soluble polyvinyl alcohol having a K value of 43 and containing 0.6% by weight of residual acetyl groups and 3% by weight of bound oxyethyl groups was obtained.

EXAMPLE 14.

Preparation of a polyvinyl alcohol containing units of an oxyethylated stearic acid:

In the manner described in the first part of Example 1 a graft polymer was prepared from

94 parts of vinyl acetate,
5 parts of oxyethylated stearic acid (formed by reacting 1 mole of stearic acid with 30 moles of ethylene oxide) and
1 part of dibenzoyl peroxide.

Hydrolysis or alcoholysis:

44.6 parts of the above-mentioned graft polymer dissolved in 178.4 parts of methanol

were introduced at 20°C. while stirring into a solution of

12.5 parts of methanolic sodium hydroxide solution of 15% strength by weight.

The mixture was stirred for about 3 hours. Then the product was filtered off with suction from the mother liquor, washed with methanol until free from alkali and dried in vacuo at 35°C. A modified polyvinyl alcohol which was readily soluble in water and contained 4% by weight of bound oxyethyl groups was obtained.

Example 15.

Preparation of a modified polyvinyl alcohol containing carboxyl groups and residual acetate groups:

In the manner described in the first part of Example 1 a graft polymer was prepared from

400 parts of vinyl acetate,
32 parts of crotonic acid,
40 parts of polyethylene glycol having a molecular weight of 15,000 and
6 parts of dibenzoyl peroxide.

Hydrolysis or alcoholysis:

74 parts of methanolic sodium hydroxide solution of 5% strength by weight

were introduced at 25°C., while stirring, into

350 parts of the above-mentioned graft polymer dissolved in
641 parts of methanol and
9 parts of water.

After the beginning of the formation of the thick phase stirring was interrupted and the mass was allowed to stand for 4 hours at 30°C. Then steam was introduced into the mass, stirring was continued and the whole of the methyl acetate and methanol was distilled off; the steam distillation was terminated when the solution had a temperature of 99°C. A solution of the modified polyvinyl alcohol remained behind.

Example 16.

Preparation of a partially hydrolyzed polyvinyl alcohol containing units of polyethylene glycol:

In a vessel provided with a stirrer and a reflux condenser 300 parts of polyethylene glycol having a molecular weight of 25,000 were melted at 70°C.

A solution of

1,700 parts of vinyl acetate and
16 parts of dibenzoyl peroxide

was introduced slowly and while stirring into the aforesaid polyethylene glycol. The rate of introduction was determined by the rate of polymerization. Care had to be taken that a certain excess of the monomer was always present in the reaction chamber.

Immediately after the introduction of the aforesaid solution,

600 parts of methanol

were slowly added. When the exothermic polymerization was finished, polymerization was completed while stirring for 4 hours at a temperature within the range of 80 to 90°C. under an internal pressure of about 1 atmosphere (gauge).

Hydrolysis or alcoholysis:

The above-mentioned solution of the graft polymer was diluted in the same reaction vessel with

3,660 parts of methanol and
514 parts of water and
1,900 parts of methanolic sodium hydroxide solution of 5.03% strength by weight

were added at 20°C., while stirring. After the formation of the thick phase, stirring was interrupted and the mass was allowed to stand for 4 hours at 31°C.

Subsequently steam was introduced into the mass, stirring was continued and the whole of the methyl acetate and methanol was distilled off, the distillation being terminated when the solution had a temperature of 99°C., the refluxing operation having been changed into a distilling operation.

A clear solution of the modified polyvinyl alcohol remained behind.

After having been dried in the air and being exposed for 1 hour to a temperature of 100°C., a film cast from the aforesaid solution was clear, soft and capable of being heat sealed. Even in cold water it dissolved very quickly and without leaving residues.

Analysis:

Content of acetyl groups	9.3%
content of oxyethyl groups	28.0%
content of polyvinyl alcohol	53.1%

EXAMPLE 17.

Preparation of a polyvinyl alcohol containing units of an oxyethylated polypropylene glycol containing nitrogen:

In the manner described in the first part of Example 1 a graft polymer was prepared from

89 parts of vinyl acetate,
10 parts of an oxyethylated polypropylene glycol containing nitrogen and having the following constitution:

$$\begin{matrix} H(OC_2H_4)_Y(OC_3H_6)_X \\ H(OC_2H_4)_Y(OC_3H_6)_X \end{matrix} > N{-}CH_2CH_2{-}N < \begin{matrix} (C_3H_6O)_X(C_2H_4O)_YH \\ (C_3H_6O)_X(C_2H_4O)_YH \end{matrix}$$

X = 5
Y = 216

and 1 part of dibenzoyl peroxide.

Hydrolysis or alcoholysis:

At 21°C.
14 parts of a methanolic sodium hydroxide solution of 15.1% strength by weight

were introduced, while stirring, into a solution of

50 parts of the above-mentioned graft polymer in
200 parts of methanol.

Stirring was continued for 4 hours.

The modified polyvinyl alcohol that had formed was filtered off with suction, washed with methanol until free from alkali and dried in vacuo at 40°C.

EXAMPLE 18.

Preparation of a polyvinyl alcohol containing units of a polyethylene glycol and its partial acetalization:

In the manner described in the first part of Example 1 a graft polymer was prepared from

160 parts of vinyl acetate,
40 parts of polyethylene glycol having a molecular weight of 25,000 and
4 parts of dibenzoyl peroxide.

Acid hydrolysis or alcoholysis:

A solution of

247 parts of the above-mentioned graft polymer in
317 parts of methanol and
142 parts of methyl acetate

was introduced, while stirring, into a solution of

21.4 parts of sulphuric acid of 80% strength by weight in
22.0 parts of methanol.

The mixture was stirred for 20 hours at 53°C.

After about 10 hours
9.3 parts of acetaldehyde

were added to the mixture. Measures had to be taken to prevent the acetaldehyde from volatilizing (the apparatus had to be tight and the reflux condenser to be cooled well).

After the reaction the modified polyvinyl alcohol that had formed was washed with methanol in a centrifuge until it was free from acid.

The product, while still moist with methanol, was treated with steam in a vessel provided with a stirrer. During this operation all the methanol was distilled off and replaced by water.

An aqueous solution of a partially acetalized modified polyvinyl alcohol remained behind.

Foils cast from this solution were soft and very readily soluble in water.

Subject to the foregoing disclaimer WHAT WE CLAIM IS:—

1. A process for the manufacture of a water-soluble modified polyvinyl alcohol as hereinbefore defined, wherein a graft-polymer, prepared in a homogeneous phase from one or more vinyl esters and one or more polyalkylene glycols, is subjected to an alkaline or acid hydrolysis or alcoholysis.

2. A process as claimed in claim 1, wherein the graft-polymer used is a co-polymer obtained from vinyl ester together with one or more compounds co-polymerisable therewith.

3. A process as claimed in claim 1 or 2, wherein the graft-polymer used contains a polyalkylene glycol component constiuting 0.1 to 50 per cent by weight thereof.

4. A process as claimed in any one of claims 1—3, wherein the graft-polymer used is derived from a polyethylene glycol.

5. A process as claimed in any one of claims 1—3, wherein the graft-polymer used is derived from a polypropylene glycol or higher homologue thereof.

6. A process as claimed in any one of claims 1—3, wherein the graft-polymer used is derived from one or more oxyethylated polypropylene glycols.

7. A process as claimed in any one of claims 1—3, wherein the graft-polymer used is derived from one or more polyalkylene glycols one or both terminal hydroxyl groups of which are etherified or esterified, or one or both hydroxyl groups of which are sub-

stituted by mono- or polyfunctional amines or amides, or from a reaction product of a polyalkylene glycol with a mono- or polyisocyanate.

8. A process as claimed in any one of claims 1—3, wherein the graft-polymer used is derived from one or more polyalkylene glycols that are organically substituted.

9. A process for the manufacture of a water-soluble modified polyvinyl alcohol, conducted substantially as described in any one of the Examples herein.

10. Water - soluble modified polyvinyl alcohols, when made by the process claimed in any one of claims 1—9.

ABEL & IMRAY,
Agents for the Applicants,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.